

## ***In Situ* Mn K-edge XANES of Mn-Containing Catalysts**

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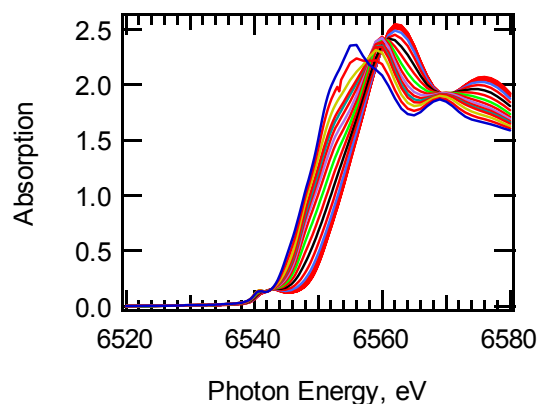
Beamline(s): X18B

**Introduction:** Unsupported and supported manganese oxides are known to be active catalysts in numerous chemical processes, including CO oxidation, oxidative coupling of methane, and selective catalytic oxidation of ethylbenzene. The  $\text{MnO}_x$  catalytic activity has been attributed to the capability of Mn to form several oxides e.g.  $\text{MnO}_2$ ,  $\text{Mn}_2\text{O}_3$ ,  $\text{Mn}_3\text{O}_4$ , or  $\text{MnO}$ , and to store and provide oxygen selectively from its lattice. Thus, the ability to measure and quantify the Mn oxidation state under reaction conditions is paramount to understanding the activity of such catalysts. The XANES of Mn is known to be sensitive to such changes, and we have used this to monitor the Mn oxidation state *in situ*.

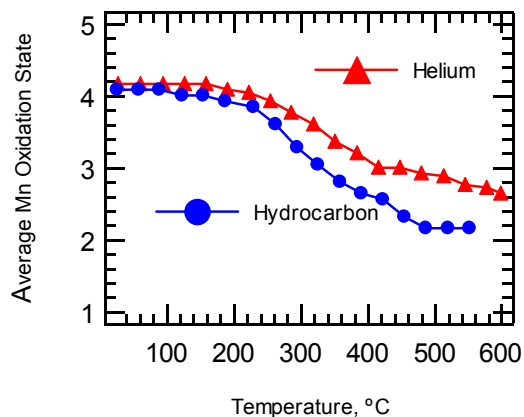
**Methods and Materials:** Temperature programmed XANES (TP-XANES) data were collected at the Mn K-edge of series of Mn oxide materials. Spectra were collected while ramping the temperature of the sample in a flow of either He or hydrocarbon. Using known reference compounds of Mn, the average Mn oxidation state was extracted for each sample as a function of temperature.

**Results:** Fig. 1 shows a set of TP-XANES at the Mn K-edge for hollandite,  $\text{KMn}_8\text{O}_{16}$ , as the sample is heated in a flow of He from room temperature to 600°C. There is autoreduction of the sample, indicating that the Mn is not stable under these conditions. Figure 2 shows the average Mn oxidation state for the hollandite sample in both the He and hydrocarbon as a function of temperature. As can be seen, while there is autoreduction of the sample, the average Mn oxidation state is lower in the flow of hydrocarbon, ending up as  $\text{Mn}^{2+}$  by 500°C. Similar data were collected on several Mn oxide materials, in a variety of atmospheres. These data were correlated with the relative activity and selectivity of the catalysts in the partial oxidation reaction. A good correlation was found between the structure of the Mn oxide, the activity, and the stability to reduction.

**Conclusions:** *In situ* Mn K-edge XANES is a powerful tool for extracting the average Mn oxidation state in Mn-containing catalysts. These data are being used to guide catalyst development for this class of catalyst.



**Figure 1.** TP-XANES spectra of hollandite,  $\text{KMn}_8\text{O}_{16}$  in a flow of He as the sample is heated from 25°C to 600°C.



**Figure 2.** Average Mn oxidation state of hollandite in He and hydrocarbon flow as a function of temperature.